VACUUM PYROLYZED TIRE OIL AS A COAL SOLVENT

Edward C. Orr, Yanlong Shi, Qin Ji, Larry L. Anderson, and Edward M. Eyring
Department of Chemistry and Department of Chemical and Fuels Engineering,
University of Utah, Salt Lake City, UT 84112

Introduction

Recent interest in coprocessing coal with hydrogen rich waste materials in order to produce liquid transportation fuels has given rise to interesting twists on standard coal liquefaction.[1-5] In general, coprocessing coal with a waste material has been approached with the idea that the waste material would be mixed with the coal under liquefaction conditions with little or no preliminary processing of the waste material other than shredding into smaller size particles. Mixing the waste material with the coal would occur in the primary stage of liquefaction. The primary stage would accomplish the dissolution of the coal and breakdown of the waste material. The products would then be introduced into the secondary stage where uprgading of product would occur.

Recent work with waste rubber tires directly coprocessed with coal has shown that this is a feasible scheme, but that additonal pretreatment of the tires is beneficial to the coprocessing. This additional step is the vacuum pyrolysis of the waste rubber tire to yield an oil that is highly aromatic. The vacuum pyrolysis of the waste rubber tires is also beneficial in separating out the carbon black and ash from the volatile constituents. It has been shown that the breakdown of waste rubber tires during vacuum pyrolysis produces polyaromatic hydrocarbons.[6] Polyaromatics are known to be beneficial in coal liquefaction.[7-9] The present paper explores the usefulness of oil derived from pyrolysis of waste rubber tires as a reactant in a coal coprocessing scheme or as a coal liquefaction solvent.

Experimental

Blind Canyon (Utah) coal (DECS-6, -60 mesh) (**BC6**) was obtained from the Penn State Coal Sample Bank and stored under nitrogen at 0 °C. Oil obtained from vacuum pyrolysis of waste rubber tires (**PTO**≡pyrolyzed tire oil) was produced by Conrad Industries, Chehalis, WA. The **PTO** was stored under ambient conditions. GC-MS analysis of the **PTO** was completed on a Hewlett Packard 5890 series II gas chromatograph coupled to a Hewlett Packard 5971 Mass spectrometer. A J & W 100 meter long DB-1 column was used for the GC-MS analyses. Elemental analyses were completed by Atlantic Microlabs, Norcross, Georgia. The precursor catalyst (ammonium tetrathiomolybdate, Aldrich) was used as received to impregnate the **BC6** from aqueous solution by the incipient wetness technique to obtain a 1 % by weight loading of the catalyst. The catalyst was added to the **PTO** in solid, dry form to achieve a 1 % by weight presence of the catalyst. The **BC6**/catalyst mixture was vacuum dried for two hours at 100 °C to remove all moisture. The **PTO/BC6** samples were placed directly in 27 cm^3 tubing reactors, purged with N_2, and pressurized to the pressure of interest. Pressures reported are for H_2 or N_2 and are initial pressures at room temperature before immersion in the sandbath. Reactors were heated by a fluidized sandbath held at various reaction temperatures. The tubing reactors were shaken vertically at 160 rpm for the duration of the experiment, removed and allowed to cool at room temperature for 5 minutes, and then quenched in cold water. Reaction products and solids were removed and extracted with tetrahydrofuran (THF). The THF was removed with a rotary evaporator, and the THF soluble portion was dried under vacuum for two hours and weighed. The THF insoluble residue remaining in the soxhlet extractor thimble was also dried for two hours under vacuum. The sum of the THF solubles and the THF insoluble residue, corrected for ash, was subtracted from the initial coal mass (daf) and solvent mass to calculate the total gas produced. Total conversion was defined as the sum of the gas and THF solubles. The dried THF solubles were then extracted with cyclohexane. The cyclohexane was removed from the oil sample using a rotary evaporator. The cyclohexane insoluble residue is referred to as asphaltenes. The cyclohexane soluble portion is referred to as oil. EPMA samples were prepared by grinding the THF insoluble portions and mixing with Petropoxy 154 (Pullman, Washington). The plug was polished with

a syntron diamond paste polisher for eight hours. Micrographs were obtained using a CAMECA Model SX-50 electron microprobe (Courbevoie, France). Two different micrographs are presented: secondary electron micrographs (SEM) and the characteristic X-ray micrograph for specific elements of interest. (All micrographs shown are for a 50 μm x 50 μm field of view).

Results

In Table 1 the analysis of the **BC6** is reported. Table 2 contains elemental analysis results for the **PTO**. The NMR results indicate the **PTO** is highly aromatic. The GC-MS analysis of the **PTO** indicated the presence of benzene, methylated forms of benzene, naphthalene, methylated forms of naphthalene, anthracene, methylated forms of anthracene, phenanthrene, methylated forms of phenanthrene, pyrene, methylated forms of pyrene, and naphthacene. These results are similar to what Williams and Taylor found for oil derived from the vacuum pyrolysis of waste rubber tires.[6]

Figure 1 contains the product yields based on the original coal (daf) and **PTO** masses. The data show good overall total conversion for the **PTO/BC6** mixtures. The results indicate that a 30 to 40 minute heating period is optimum for maximizing the conversion of **BC6/ PTO** with molybdenum catalyst present under a hydrogen atmosphere at 430 °C. Initial conversion is suprisingly high at 10 and 20 minutes. This may indicate that the **PTO** is very effective in solubilizing the coal. In all samples, charring was observed, but charring was more significant in the 50 and 60 minute samples. The significant charring is probably due to the **PTO**. The polyaromatic molecules are char precursors, thus it is not surprising that charring increased with reaction time.

Figure 2 shows the yields based only on coal. These values were calculated on the assumption that **PTO** is only present in the products as gas and oil. Therefore we can subtract out 50 % of the gas and oil and double the remaining conversion value to obtain the coal total conversion. From the new total conversion we subtract twice the amount of asphaltenes in order to obtain the new gas and oil values. This assumes no **PTO** forms char, which is very unlikely, but this permits an approximate calculation of the amount of coal that was actually converted. Thus, it could be predicted that at 30 minutes 92 % of the coal would be converted into gas, oil, and asphaltenes.

Table 3 contains the carbon and hydrogen percentages for the oils, asphaltenes, and char/ash produced from the above reactions. The carbon and hydrogen values were converted to molar values to obtain carbon/hydrogen ratios. The oil quality remained constant throughout the six time periods.

In past work, it was found that Electron Probe Microanalysis (EPMA) was useful in spotting the location of catalysts and metals in coal.[10-12] EPMA is a qualitative tool for determining the degree of dispersion of metal catalysts in coal particles.

The EPMA data in Fig. 3 show a coal particle taken from a sample which containsed **BC6** coprocessed with **PTO** at 430 °C for only 20 min. For the coal particle, a secondary electron micrograph (SEM), a sulfur X-ray image, and a molybdenum X-ray image are shown. The SEM image and sulfur X-ray image are presented to show the location of the coal particle. The **BC6** contains approximately 0.4 % by weight sulfur which the EPMA detects. Fresh coal contains no molybdenum, therefore detection of molybdenum by the EPMA indicates the presence of catalyst. The detection limit of the EPMA for molybdenum is approximately 200 ppm. Thus catalyst may be present in samples even though it may not be detected by EPMA.

The molybdenum micrograph in Figure 3 indicates the presence of the molybdenum catalyst in the coal particle. It is somewhat surprising to find catalyst inside the coal particle at such an early time in the liquefaction period. In previous unpublished work we found that when **BC6** was reacted at 350 °C without any solvent and the molybdenum was not incorporated into the coal matrix until 50 to 60 minutes of coprocessing had occurred. The high total conversion

observed after 20 minutes for the **PTO/BC6** system indicates that dissolution and thermal cracking of the coal occurred rapidly. **PTO** probably induces swelling thus allowing for greater dispersion of the catalyst throughout the coal particles. This suggests that increased dispersion of the molybdenum catalyst observed in the coal particles by EPMA may be partially responsible for the high conversion values.

Conclusion

Tire oil obtained by vaccum pyrolysis of waste rubber tires is better than shredded tires for coprocessing with coal. The **PTO** appears to be a good dissolution solvent for the coal and an effective hydrogen donor. EPMA data indicate that the solvent readily enters the coal matrix thus aiding catalyst dispersion.

References

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Table 1 Analysis of Blind Canyon DECS-6 Coal*

Proximate	Percentage
% Ash	5.84
% Volatile	44.50
% Fixed Carbon	49.66
Ultimate	Percentage
% Carbon	81.28
% Hydrogen	6.24
% Nitrogen	1.55
% Sulfur	0.42
% Oxygen	10.5

* Penn State Coal Sample Bank

Table 2 Elemental Analysis of Oil Derived From The Vacuum Pyrolysis of Waste Rubber Tires

Element	Percentage
Carbon	87.7
Hydrogen	11.0
Nitrogen	0.3
Sulfur	0.6

Figure 1 Conversion results for Blind Canyon DECS-6 and oil obtained from the pyrolysis of waste rubber tires. Coprocessing was carried out in tubing reactors at 430 °C under hydrogen gas with a molybdenum catalyst present. The ratio of coal to oil was 1:1 by weight.
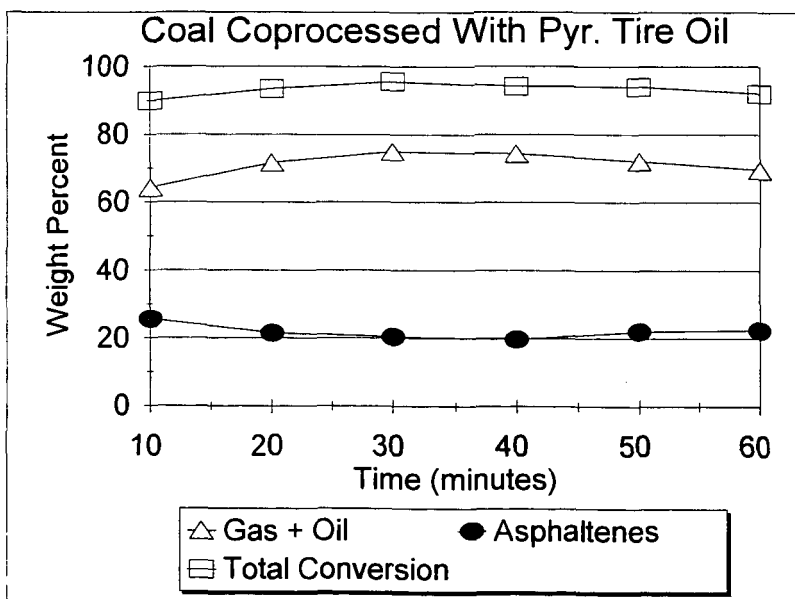
Figure 2 Conversion results for Blind Canyon DECS-6. Coprocessing was carried out in
tubing reactors at 430 °C under hydrogen gas with a molybdenum catalyst present. The ratio
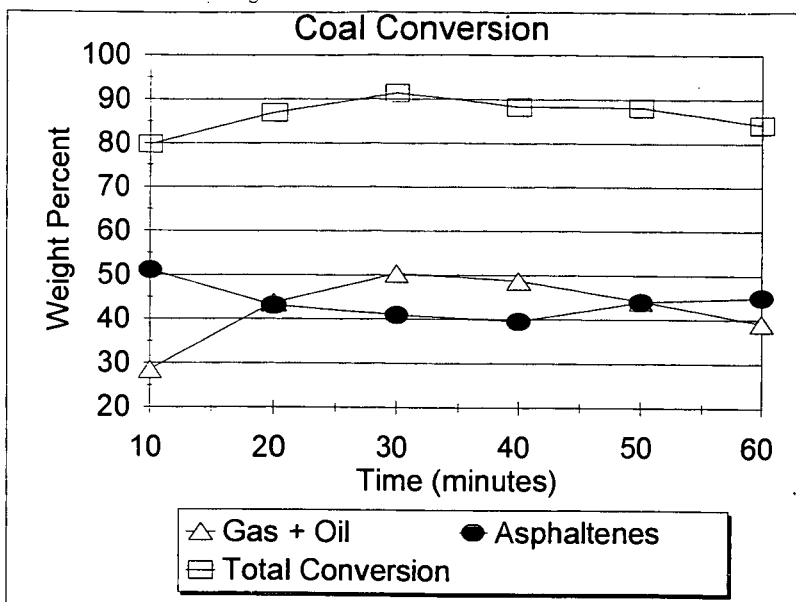of coal to oil was 1:1 by weight.

Coal Conversion

Legend:
△ Gas + Oil   ● Asphaltenes
⊟ Total Conversion

Table 3 Carbon and Hydrogen Analysis of Oil, Asphaltenes, and Char/Ash

|	Oil	Asphaltenes	Char/Ash
10 Minutes			
Carbon	86.8	84.3	57.6
Hydrogen	8.6	5.8	3.2
Molar Ratio	.8	1.2	1.5
20 Minutes			
Carbon	86.0	85.6	53.4
Hydrogen	8.4	5.5	2.8
Molar Ratio	.9	1.3	1.6
30 Minutes			
Carbon	84.3	87.1	43.0
Hydrogen	8.3	5.6	2.2
Molar Ratio	.9	1.3	1.6
40 Minutes			
Carbon	86.4	86.9	38.9
Hydrogen	8.5	5.5	2.0
Molar Ratio	.9	1.3	1.6
50 Minutes			
Carbon	84.9	87.6	56.0
Hydrogen	8.3	5.4	2.9
Molar Ratio	.9	1.4	1.6
60 Minutes			
Carbon	85.1	87.7	59.9
Hydrogen	8.1	6.0	2.8
Molar Ratio	.9	1.2	1.8

Figure 3
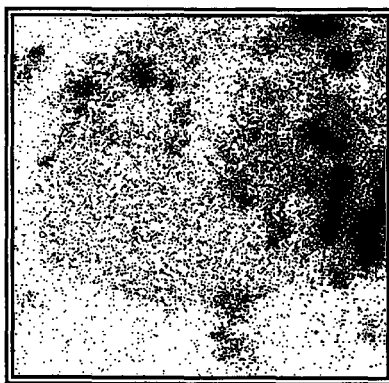**Blind Canyon DECS-6 coal in pyrolyzed tire oil**
1 % ammonium tetrathiomolybdate
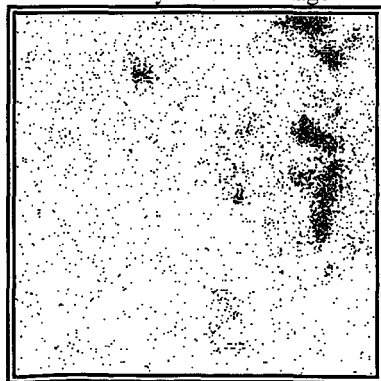Hydrotreated for 20 minutes, 430° C, 1000 psig (cold) H_2
EPMA micrograph dimensions (50 μm x 50 μm)
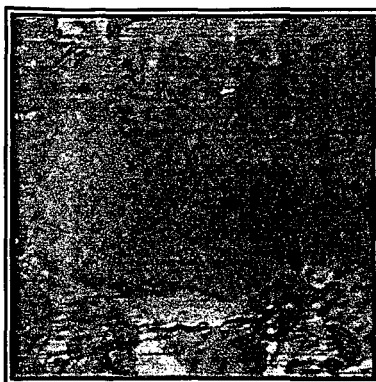
Secondary Electron Image

Sulfur K_α

Molybdenum L_α